



# 2015

## APS/CNM Users Meeting



# CNM POSTER ABSTRACTS





## Chemistry

C-1

### X-ray Nanodiffraction Study of the Delithiation Mechanism of $\text{LiFePO}_4$ Single Particles

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Lithium iron phosphate ( $\text{LiFePO}_4$ ) has received much interest as a cathode material on account of its good reversibility, low toxicity, thermal stability, and high material abundance [1]. However, there are some key fundamental drawbacks in that it is a poor ionic and electronic conductor, which are apparent in the rate performance. Understanding the intercalation mechanism will provide insight on some of the core limitations of this material. Two-phase and solid solution mechanisms have been proposed, but details on the transformation at the single particle level remain elusive [2]. X-ray nanodiffraction measurements on single particles were carried out to produce direct observations of the electrochemical reaction at a fundamental level.

Argonne National Laboratory's Advanced Photon Source boasts a hard x-ray nanoprobe beamline that has a very high spatial resolution of  $\sim 30$  nm [3]. Traditionally, this beamline has been used to study thin films. Here, its power was harnessed to observe single microcrystals in a powder sample. Two-dimensional area maps were taken of one particle each of  $\text{LiFePO}_4$ ,  $\text{FePO}_4$ , and an intermediate average powder composition  $\text{Li}_{0.5}\text{FePO}_4$ , which contained both fluorescence and diffraction data. Combining the fluorescence and diffraction data, the phases involved in the  $\text{LiFePO}_4$ - $\text{FePO}_4$  transformation were identified within the particle from the distance between lattice planes, calculated with Bragg's Law. Additionally, strain and inhomogeneities were also identified. Visualizing these phenomena on the single particle level and how they correlate to each other sheds light upon the electrode operation and how battery failure ultimately occurs. This information may lead to advancements in this material as well as those with similar structures.

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C-2

### Conjugated Bridge Effects on Triplet Generation in Ladder-type Perylene Dimers

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Understanding the design of triplet generating chromophores is key to developing the next generation of optoelectronic organic materials. For example, long triplet exciton diffusion lengths can improve photocurrent in photovoltaic devices, and the generation of multiple triplet excited states from a single photon absorption event can potentially raise device efficiency above the Shockley-Queisser limit. We are investigating the photophysical properties of a series of ladder-type conjugated perylene diimide dimers using transient absorption spectroscopy on subpicosecond to microsecond timescales across the entire visible spectrum. These experiments show the generation of excited triplet states lasting tens of microseconds on the first of several molecules in the series. Here we investigate the effects of changes to the ladder-type bridge on the triplet generation properties of two such systems.

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## Environmental Science & Geology

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C-3

### **Preliminary Assessment of Microstructures on Siliceous Microfossils in Subglacial Lake Whillans, West Antarctica**

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The WISSARD Project recovered sediments from a subglacial lake beneath the Whillans Ice Stream which drains the West Antarctic Ice Sheet (WAIS) into the Ross Ice Shelf. Sediment samples from Subglacial Lake Whillans (SLW) provided the first look at a subglacial ecosystem that is isolated from the ocean and atmosphere. Analysis of the sediments revealed a thriving and diverse community of microbes such as extremophile bacteria, with a likely food source of fossil carbon and other nutrients derived from marine microfossils deposited during times when the ice sheet was in retreat and this was an open marine embayment. A variety of diatom ages are present, but the dominant age of the marine deposits is late Miocene (ca. 8 million years before present). The fossils include sponge spicules and diatoms.

We used the FEI Quanta 400F (E) SEM in association with the Center of Nanoscale Materials to analyze these fossils to document preservational effects of both subglacial mechanical shearing and microbial utilization of microfossil-based organic matter on the fossils. Mechanical degradation is evident by fresh fracture features, whereas microbial processes result in etching and pitting of the fossils. We find that diatoms are mechanically fragmented but lack dissolution features, whereas, sponge spicules have evidence of chemical etching features that we attribute to microbial attack, in addition to mechanical breakage. A microbial cell was observed on one of the spicules further supporting our hypothesis that the fossil sponge spicules provide a significant nutrient source for the microbial community beneath the WAIS.

## Materials Science

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C-4

### **Origins of Anisotropy in the Magnetic Structure of Artificial Spin Ice Lattices**

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Artificial spin ice lattices are a two-dimensional analogue to spin ice crystals. The larger length scales of the artificial systems allow for their magnetic frustration behavior to be observed at room temperature. Traditionally, artificial spin ice lattices are patterned in thin films using electron-beam lithography because the elements that make up the lattice need to be small if they are to remain single domain. However, such fabrication is difficult to perform when the thin films have been deposited onto transparent membranes on TEM grids. Therefore, for those lattices whose elements remain single-domain at larger sizes, focused-ion beam (FIB) patterning represents a better alternative. In order to explore the origins of observed anisotropy in the lattices, Lorentz transmission electron microscopy has been used to obtain quantitative maps of the magnetization in square spin ice lattices FIB patterned in Ni<sub>80</sub>Fe<sub>20</sub> (Permalloy) thin films. Our results have shown that although FIB patterning has an effect on the grain size of the Permalloy at the edges of the patterned regions, the anisotropy that is observed is the result of pre-existing anisotropy in the Permalloy film, rather than an effect introduced by the FIB patterning. Our results thus suggest that FIB patterning is an effective method for fabricating larger-scale artificial spin ice lattices.

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C-5

## Evolutionary Algorithm Search for Global Minimum Structures of Au Nano-clusters

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Gold nano-clusters are considered for applications such as optoelectronics, bio-recognition, and catalysis. In spite of their enticing potential, the atomic structures of very small (number of atoms <15) Au clusters are still elusive. For instance, there is ongoing debate on the critical cluster size, reportedly between 7 to 15 atoms, beyond which globular -3D- structures become more stable compared to planar -2D- ones. Furthermore, we found that some isomers at a given cluster size are energetically very close (<10 meV/atom), the reasons of which should be sought in finer details of electronic structures rather than mere differences in the number of dangling bonds at the edges or surfaces. Here, we present high throughput density functional theory calculations (DFT) coupled with a global structural optimization scheme using genetic algorithm (GA) to identify the ground state structures of Au nano-clusters near the critical cluster size. By investigating the electronic and vibrational properties of the low energy structures, we explore fundamental changes that drive the structural transformations.

C-6

## Bond Order Potential to Capture Size-dependent Dimensionality Effects in Au Nanoclusters

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Gold nanoclusters, owing to their exceptional chemical, optical, and electronic properties, hold promise in a wide range of applications, such as optoelectronics, bio-recognition, and catalysis. Interestingly, Au nanoclusters are known to exhibit a diverse variety of structural configurations including planar, hollow cages, chiral tubes, and bulk-like pyramids or icosahedra. Despite these earlier observations, a fundamental understanding of the atomic structure of Au nanoclusters is still lacking — in particular, dependence of the structure of an  $Au_n$  cluster on its size  $n$  (i.e., number of atoms). For instance, there is an open debate on the critical cluster size  $n_c$  beyond which globular isomers become energetically preferable over planar ones, with reported values of  $n_c$  ranging from 7 to 15. Furthermore, the knowledge of structural transitions between energetically close isomers ( $\sim 20$  meV/atom) at a given size is still in its infancy. Global optimization and molecular dynamics (MD) simulations via empirical force fields (EFFs) provide an ideal route to address these issues. However, none of the available EFFs can adequately capture the dimensionality effects from bulk to sub-nanometer clusters. Popular pairwise Au EFFs, such as Morse, or those that account for multi-body effects via an embedding function (e.g., EAM, MEAM) tend to artificially over-stabilize bulk-like isomers. Here, we employed genetic algorithms to parameterize a bond-order potential based on Tersoff functional form by training against cohesive energies of representative clusters and condensed bulk phases of Au computed by density functional theory (DFT) calculations. This new EFF was found to be capable of describing the diverse range of structures of Au nanoclusters consistent with previous reports (e.g., planar structures circa  $Au_{13}$ , hollow cage at  $Au_{14}$ , and compact pyramid at  $Au_{20}$ ). Furthermore, we employed long-time MD simulations with this EFF to identify the mechanisms governing agglomeration of clusters. Finally, our new hybrid EFF, which can describe Au clusters well in the nanometer length scale; this will open doors to structure prediction of technologically relevant mid-size Au clusters ( $n=20-80$ ) that are not tractable by DFT alone.

C-7

**IrO<sub>2</sub> Surface and Nanostructure Stability from First Principles and Variable Charge Force Field Calculations****Fatih G. Sen<sup>1</sup>, Alper Kinaci<sup>1</sup>, Badri Narayanan<sup>1</sup>, Michael J. Davis<sup>2</sup>, Stephen K. Gray<sup>1</sup>, Subramanian K.R.S. Sankaranarayanan<sup>1</sup>, and Maria K. Chan<sup>1</sup>**<sup>1</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne IL 60439<sup>2</sup>Chemical Sciences and Engineering, Argonne National Laboratory, Argonne IL 60439

IrO<sub>2</sub> is one of the most efficient water-oxidation electrocatalysts and can also act as a photocatalyst for the water splitting reaction when used in the form of nano-sized clusters. The structure and surface properties of nanoclusters greatly influence the photocatalytic properties of IrO<sub>2</sub>, and atomistic scale understanding of these properties is essential to elucidate the photocatalytic mechanisms of IrO<sub>2</sub>. Here, we carried out first principles calculations based on spin polarized density functional theory (DFT) including spin-orbit coupling and the Hubbard *U* correction on the bulk and surface structures of IrO<sub>2</sub>. The stability and electronic structure of low index rutile (100), (001), (110) and (101) surfaces of IrO<sub>2</sub>, were studied. The relative surface energies were obtained as (110) < (101) < (100) < (001). The equilibrium shape of IrO<sub>2</sub> nanoparticles was deduced using a Wulff construction. In order to study the structural stability of IrO<sub>2</sub> nanoclusters and the long time-scale dynamics of IrO<sub>2</sub> polymorphs larger than about 2 nm in diameter, we developed the first empirical interatomic potential (force field) for IrO<sub>2</sub> based on Morse functional form coupled with a variable charge method (QEeq). The Morse+QEeq parameters were optimized using an evolutionary algorithm with respect to a DFT training set, and was shown to be successful in predicting bulk and surface properties of rutile IrO<sub>2</sub> and various polymorphs including anatase, brookite, columbite and pyrite derived from DFT calculations. Pressure induced phase transformations of bulk IrO<sub>2</sub> polymorphs were reported and thermodynamically stable phases of IrO<sub>2</sub> at nano-scale were obtained using the surface energies of stable polymorphs. Our results will shed light on the development of stable nanoscale IrO<sub>2</sub> electrocatalysts and photocatalysts that can efficiently utilize solar energy for water splitting reaction.

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**Nanoscience and Nanotechnology**

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C-8

**New Fabrication Techniques for Cryogenic Micro-calorimeters****Thomas Cecil, Lisa Gades, Tim Madden, Daikang Yan, and Antonino Miceli**

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Cryogenic micro-calorimeters provide the highest energy resolution of any solid state x-ray detectors. At APS we have been focused on developing a superconducting technology called thermal kinetic inductance detectors (TKIDs), which is a resonator-based technology. We present the results of several new fabrication efforts at CNM to increase the performance of TKIDs: new alloys of WSi<sub>6</sub> with tunable T<sub>c</sub> from 500mK to 5K, sloped SiN etching via resist reflow, and deep silicon etching of x-ray apertures. These techniques allow us to reduce thermal fluctuation noise due to a lower T<sub>c</sub> resonator material, reduce TLS noise by removing the SiN underneath the resonator capacitor, and limiting spurious x-ray pulses by blocking x-ray absorption in the device wiring with the use of the aperture.

C-9

**Lithium Sulfur Batteries as Energy Storage Devices****Lin Chen**

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The lithium sulfur battery as an excellent alternative for energy storage devices has attracted extensive interests. Herein, we adopted a facile approach to synthesize the Li<sub>2</sub>S @ nitrogen-doped carbon, which contains the active



materials as high as 72%. With SEM and EFTEM characterizations, the size of this composite is about 400 nm, and has a very great core-shell structure for protecting lithium polysulfides from dissolutions to electrolytes. The doped nitrogen revealed by XPS facilitates electrons diffusion in the battery system and thus enables a superior electrochemical reaction condition. The  $\text{Li}_2\text{S}$  encapsulated by nitrogen-doped carbon can deliver extremely high specific capacity of 1029 mA h/g at 0.2 C and retain 652 mA h/g even after prolonged 100 cycles.

## C-10

### ZnO Functionalization of Surface Pre-treated Multi-walled Carbon Nanotubes for Methane Sensing

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Bare carbon nanotubes (CNTs) are insensitive towards most gases due to poor bonding between the chemically inert graphitic surface and different compounds they are exposed to. Consequently, for gas sensing applications, functionalization of CNTs with reactive compounds is required. By introducing surface pre-treatments prior to functionalization, the affinity of the functionalizing species is enhanced, enabling the fabrication of highly sensitive CNT chemiresistor-based sensors.

Atomic layer deposition (ALD) allows precise, uniform and conformal deposition of oxide coatings on geometrically complex substrates such as MWCNTs [1]; thus offering a suitable route for the functionalization of MWCNTs for gas sensing applications. Motivated by the energetically favorable electron transport in ZnO-MWCNT junctions [2], we have performed ALD of ZnO for functionalizing  $\text{O}_2$  plasma and UV- $\text{O}_3$  treated MWCNTs. Diethylzinc ( $(\text{C}_2\text{H}_5)_2\text{Zn}$ ) was used as an ALD precursor. Deposition was performed at three different temperatures, 175, 200 and 225°C, with an Arradance Gemstar ALD tool. Transmission electron microscopy (TEM) images show uniform deposition of ZnO nanoparticle (NP) layers on the MWCNTs. At ALD temperature of 175°C and 200°C the average NP size was found to be 7.2 nm (standard deviation, SD, 1.18 nm) and 10.8 nm (SD 1.81 nm) respectively. The higher resolution TEM image illustrates the wurtzite structure of the ZnO-NP and its good crystalline quality. The interplanar spacing of 2.8Å, 2.68Å and 2.48Å correspond to <100>, <002> and <101> planes of ZnO [3]. Raman spectroscopy also suggests good crystal quality of ZnO-NP. The chemiresistor sensors based on ZnO functionalized MWCNTs were used to detect ppm level concentrations of methane in zero air at room temperature.

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C-11

**Nanostructure Electrodes for Perovskite Solar Cells and Electrochromic Devices****Qinglong Jiang<sup>1</sup>, Xia Sheng<sup>2</sup>, Xinjian Feng<sup>2</sup>, Bing Shi<sup>3</sup>, Tao Li<sup>3</sup>, and Tao Xu<sup>1</sup>**<sup>1</sup>Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115<sup>2</sup>Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu 215123, China<sup>3</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Charge transport at the interfaces and bulk phases governs the efficiency of various heterojunction optoelectronic devices such as electrochromic cells and solar cells. Here, I will present my research works on charge transport processes in two different optoelectronic devices: nanostructured heterojunction photovoltaic cells and electrochromic devices.

Current lead halide perovskite solar cells have photoactive layer less than 600 nm due to the increment of dark current and electron transport resistance in thicker layer. TiO<sub>2</sub> nanowires have been used in perovskite solar cells and photoactive layer is as thick as 900 nm. We apply these rutile NW arrays with different length as photoanodes in perovskite solar cells and we achieved 11.7% efficiency, which is 2% (absolute value) higher than the best perovskite solar cells using nanowire as photoanode reported in the literatures [1].

Lead halide perovskite solar cells use low chemical potential, that is, high work-function ( $\phi$ ) precious metals, such as gold ( $\phi=5.1$  eV), as the back cathode to maximize the attainable photovoltage. We report herein a set of perovskite type solar cells that use nickel ( $\phi=5.04$  eV), an earth abundant element and non-precious metal, as back cathode, and achieve nearly the same open-circuit voltage as gold and an efficiency of 10.4%. This work opens a “nickel”-and-dimed (low-cost) way towards high-efficient perovskite solar cells [2].

A solid-state electrochromic (EC) device based on 3-D conductive fluorinated tin oxides (FTO) nanobeads electrodes with over 500 roughness factor was obtained. The 3-D conductive FTO nanobeads electrode reduced the driving voltage to less than 1.2 V and response time to 272 ms, in comparison 2-D flat FTO film as the electrode [3].

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[3] Jiang, Q.; Liu, F.; Li, T.; and Xu, T., Fast and low voltage-driven solid-state electrochromics using 3-D conductive FTO nanobead electrodes. *Journal of Materials Chemistry C* 2014, **2** (4), 618.

C-12

**Sequential Infiltration Synthesized ZnO Nanostructures****Leonidas E. Ocola<sup>1</sup>, Kyle Chen<sup>2</sup>, David Gosztola<sup>1</sup>, and Angel Yanguas-Gil<sup>3</sup>**<sup>1</sup>Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup>Illinois Mathematics and Science Academy, Aurora, IL 60506<sup>3</sup>Energy Sciences Division, Argonne National Laboratory, Argonne, IL 60439

We present a method of creating zinc oxide (ZnO) nanostructures that may be used for photonic applications by combining lithography and an ALD process named Sequential Infiltration Synthesis (SiS) [1]. The SiS method utilizes similar concepts of ALD with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a polymer matrix (e.g., polymethyl methacrylate or PMMA) and allow the reaction to occur inside the polymer matrix. To achieve this it is necessary to allow time for the gases to diffuse (longer exposure times and higher pressures). Although SiS has been used mainly for applications with block copolymers [1], it can be also used in conjunction with lithography.





We demonstrate that SiS process of ZnO allows the formation of ZnO throughout 270 nm of PMMA and shows we can create unusual ZnO nanostructures by combining ZnO SiS process with lithographically patterned PMMA. X-ray and photoluminescence data of SiS treated PMMA will be presented.

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## C-13

### Development Characteristics of Polymethyl Methacrylate in Alcohol/Water Mixtures

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Poly methyl methacrylate (PMMA) is the most widely used resist in electron beam lithography. This paper reports on the study of development characteristics of PMMA in methanol, ethanol and isopropanol (IPA) mixtures with water as developers. We have found that ethanol/water mixtures at a 4:1 volume ratio are an excellent, high resolution, non-toxic, developer for exposed PMMA and GL-2000 resist. Ethanol is much less hazardous than both methyl isobutyl ketone (MIBK) and IPA (traditional PMMA developers). As a developer, ethanol had been used in combination with other solvents [1] or as “95%” ethanol [2,3]. No detailed study of ethanol-water mixtures as a developer for PMMA has been previously reported as far as we have investigated.

Our results show how powerful simple lithographic techniques can be used to study ternary polymer solvent solutions when compared to other techniques found in the literature. The impact of the understanding these interactions may open doors to a new family of developers for other electron beam resists that can reduce the toxicity of the waste stream. We have already tested Ethanol:Water in 4:1 volume ratio on GL-2000-12 resists (similar to ZEP 520A) with good resolution. Contrast, resolution and Raman spectral data will be presented.

*Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.*

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## C-14

### Study of Polarization Anisotropy of Grown Cadmium Sulphide Nanowires

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Cadmium sulphide (CdS) nanowire arrays were grown using a nanoporous template via electrodeposition. Raman and PL intensity were recorded for parallel and perpendicular polarization with two orientations of the sample having light propagating parallel to the nanowire axis in one orientation and light propagating perpendicular to the nanowire axis in other orientation. Furthermore, to study orientation dependent electron phonon (EP) coupling polarized Raman spectroscopy was also performed on wurtzite CdS nanowires for different angles of the axis of nanowire (z axis) and the laser polarization. Strong peaks of different phonon modes belonging to wurtzite structured CdS nanowires were observed with different polarizations of Raman spectral studies.

The EP coupling strength is estimated by the ratio of Raman intensity of the 2 longitudinal optical (LO) phonon peak with respect to that of the 1 LO phonon peak, according to the Franck Condon approximation. Therefore, the

strongest EP coupling was observed when the polarization of the laser is parallel to the axis of the nanowire, and decreases until the polarization of the laser is perpendicular to the axis of the nanowire. The Hamiltonian function of EP coupling strength for wurtzite CdS crystals was computed for the different angles between the long axis of nanowire (z axis) and the laser polarization for comparison with experimental observations. The computed EP coupling constant decreases with the increasing angle between the axis of nanowire (z axis) and the laser polarization as observed experimentally. The Raman and photoluminescence (PL) properties were characterized for the grown CdS nanowires which showed a remarkable polarization anisotropy of 0.80 in the PL intensity, portending the possible use of these nanowire structures in polarization-based sensitive nanoscale devices for optoelectronic applications.

## C-15

### **Fabrication of Large Transition Edge Sensor Bolometer Arrays for CMB Measurements in the Upcoming SPT-3G Experiment**

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Since its discovery, the cosmic microwave background (CMB) has played a pivotal role in cosmology and particle physics. The ability to make precision measurements of the CMB is led by detector innovation. The frontier of CMB detector development is focused on improving bolometric detectors based on superconducting Transition Edge Sensors (TES). In this sense, this work presents the fabrication of large arrays of multi-chroic TES bolometers for CMB measurements using the South Pole Telescope. The resulting array of detectors, known as SPT-3G, will be the third generation CMB camera to be installed in the South Pole Telescope. It will deliver a factor of ~20 improvement in mapping speed over the current receiver, SPT-POL.

Each pixel is composed of a broad-band sinuous antenna coupled to a niobium microstrip line. In-line filters are used to define the different band-passes before the millimeter-wave length signal is brought to the respective Ti/Au TES bolometers. There are six TES detectors per pixel, which allow for measurements of three band-passes (90 GHz, 150 GHz and 220 GHz) and two polarizations. When finished, the SPT-3G camera will be composed ~2700 pixels, featuring a total of ~16000 TES bolometric detectors. The steps involved in the monolithic fabrication of these detectors arrays are presented in detail in this work. Patterns are defined using a combination of stepper and optical lithography. The misalignment between layers is kept below 200 nm. The overall fabrication process involves a total 16 steps, which include PECVD deposition, reactive and magnetron sputtering, RIE, RIE-ICP and chemical etching. To assure a good performance of the detectors, the quality of the metallic and dielectric films involved in the fabrication is controlled using both cryogenic and room temperature testing.

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C-16

## **Spectroscopic Imaging of NIR to Visible Upconversion from NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> Nanoparticles on Au Nano-cavity Arrays**

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We use spectroscopic imaging to assess the spatial variations in upconversion luminescence from NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> nanoparticles embedded in PMMA on Au nano-cavity arrays over a wide range of excitation intensities. The nano-cavity arrays support a surface plasmon (SP) resonance at 980 nm, coincident with the peak absorption of the Yb<sup>3+</sup> sensitizer. Spatially-resolved upconversion spectra show a 30X to 3X luminescence intensity enhancement on the nano-cavity array compared to the nearby smooth Au surface, corresponding to varying excitation intensities from 1 W/cm<sup>2</sup> to 300 kW/cm<sup>2</sup>, spanning the non-linear and saturation power dependence regimes. Our analysis shows the power dependent enhancement in upconversion luminescence can be almost entirely accounted for by a constant shift in the effective excitation intensity, which is maintained over five orders of magnitude variation in excitation intensity. The variations in upconversion luminescence enhancement with power are modeled by a 3-level-system near the saturation limit, and by simultaneous solution of a system of coupled nonlinear differential equations, both analyses agree well with the experimental observations. The amplification of the excitation field is independent of the emission wavelength, suggesting the enhancement in upconversion emission is due to entirely increased absorption by the Yb<sup>3+</sup> sensitizer. Analysis of the statistical distribution of emission intensities in the spectroscopic images on and off the nano-cavity arrays provides an estimate of the average enhancement factor independent of fluctuations in nano-particle density.

C-17

## **Frictional Properties of Graphene on Silica Surfaces with Nanoscale Roughness**

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Microelectromechanical systems (MEMS) devices suffer from severe wear and short lifetimes from high pressure asperity-asperity contacts due to the nature of their rough surfaces. Recently nanoscale carbon lubricants, such as graphene, have become of interest as protective surface coatings for MEMS. Here, AFM has been used to investigate the frictional properties of graphene on hydrophilic and hydrophobic nanoparticle films, which model the nanoscaled asperities found on realistic surfaces. Combined AFM and Raman microspectroscopy studies revealed that graphene is strained and partially conforms to the rough surfaces. As the number of layers increase, conformity decreases due to the bending stiffness, but increases under mechanical loading. Friction nominally decreases as a function of layer thickness, but was also found to depend on contact area of the tip and interfacial shear strain of the graphene associated with its adhesion to the substrate. Adhesion of graphene to the tip was found to depend on the degree of surface roughness and humidity.

C-18

## **Novel Approaches towards Efficient Mg Rechargeable Batteries**

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To meet surging demands for sustainable energy and clean environment, one critical requirement is to develop high-energy, safe and low-cost rechargeable batteries for electric transportation and grid energy storage. Mg rechargeable batteries (MgRBs) stand out as a promising candidate beyond lithium ion battery technologies due to high volumetric energy density, resource abundance, and the dendrite-free deposition behavior of Mg, which ensures

safe operation [1]. Many of the advantages of MgRBs originate from the divalent nature and small ionic size of Mg ions; however, these properties also render the cation too polarizing to diffuse easily in most ion-intercalation materials. We recently investigated interlayer expansion as a general and effective atomic-level lattice engineering approach to transform inactive layered intercalation hosts into efficient Mg storage materials without adverse side effects [2]. We have combined theory, synthesis, electrochemical measurements, and kinetic analysis to improve Mg diffusion behavior in MoS<sub>2</sub>, which is a poor Mg transporting material in its pristine form. The expansion boosts Mg conductivity by two orders of magnitude, effectively enabling the otherwise barely active MoS<sub>2</sub> to approach its theoretical storage capacity as well as to achieve one of the highest rate capabilities among Mg-intercalation materials. The interlayer expansion approach can be leveraged to a wide range of host materials for the storage of various ions, leading to novel intercalation chemistry and opening up new opportunities for the development of advanced materials for next-generation energy storage.

In addition, we also demonstrated the excellent stability of a high areal capacity hybrid magnesium-lithium-ion batteries (MLIBs) cell and dendrite-free deposition behavior of Mg under high current density [3]. The hybrid cell showed no capacity loss for 100 cycles with Coulombic efficiency as high as 99.9%, whereas the control cell with a Li-metal anode only retained 30% of its original capacity with Coulombic efficiency well below 90%. The use of TiS<sub>2</sub> as a cathode enabled the highest specific capacity and one of the best rate performances among reported MLIBs. Postmortem analysis of the cycled cells revealed dendrite-free Mg deposition on an Mg anode surface, while mossy Li dendrites were observed covering the Li surface and penetrated into separators in the Li cell. The energy density of a MLIB could be further improved by developing electrolytes with higher salt concentration and wider electrochemical window, leading to new opportunities for its application in large-scale energy storage.

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## C-19

### Protection of Exfoliated Black Phosphorus Transistors from Ambient Degradation

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Black phosphorus (BP), a two-dimensional phosphorus allotrope, is unique among layered nanomaterials due to its anisotropy, high carrier transport ( $\sim 1000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ), tunable band gap ( $\sim 0.3$  to  $1.5 \text{ eV}$ ), and chemical reactivity. However, the reactivity of BP leads to its chemical degradation in ambient conditions, affecting high performance applications utilizing the nanomaterial. When unencapsulated, exfoliated BP flakes degrade into oxidized phosphorus compounds, as determined by atomic force microscopy, x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, and electrostatic force microscopy measurements. Oxygen-saturated H<sub>2</sub>O is a major source of this BP oxidation, since BP flakes placed on hydrophobic substrates are observed to degrade two times faster than on hydrophilic substrates. After 48 hours in ambient, unencapsulated BP field-effect transistors (FETs) decrease in mobility and current on/off ratio by factors of 1000. Conversely, AlO<sub>x</sub> encapsulated BP FETs do not oxidize, maintaining mobilities of  $\sim 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and on/off ratios of 1000 for over four months in ambient. This strategy to protect BP against ambient oxidation will facilitate the realization of BP electronic and optoelectronic applications and augment ongoing fundamental BP research [1].

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C-21

## X-ray Absorption Spectroscopy (XAS) Study of Sorption Mechanisms of Cd(II) to Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) Nano Particles with Varying Size and pH Environment

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Natural mineral nanoparticles have gained attention due to their wide occurrence in soil and high sorption capacities for cationic and anionic contaminants influencing the mobility and transport of contaminants in the environment. This is a consequence of their small size and non-optimal surface coordination environment compared to the bulk. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a mineral whose particles are found in the nano-sized region. This study involves investigating the sorption mechanisms of the highly toxic heavy metal cadmium to hematite. Experiments were normalized to total hematite nanoparticle surface area within reaction vessels. The sorption mechanisms were investigated under different hematite particle sizes (8nm and 40nm surface area/mass normalized (SAN/MN)) and different pH environments (pH 7.5 and pH 9).

The adsorption edge experimental results suggested particles sorbed more Cd(II) as the pH environment was increased and the particle size was decreased. For the larger particles, the sorption edge was shifted to the right approximately by 1 pH unit. X-ray absorption near edge structure (XANES) results on 8 nm nanoparticles and the 40 nm SAN at pH 7.5 indicated the presence of similar coordination environment around the absorbing Cd atom. Cd was adsorbed to 8 nm particles at pH 7.5 but did not form a precipitate whereas at pH 9, minor amounts of CdCO<sub>3</sub> and CdO were present. When experiments were normalized to hematite surface area, particle size did not substantially affect the sorption mechanism at pH 7.5. However, at pH 9 a combination of CdCO<sub>3</sub> precipitate and adsorption complex(es) were formed of which contribution from the precipitate was larger. When experiments were normalized to hematite mass, more Cd precipitation was observed in larger nano particles at both pH values. This is most likely due to the presence of fewer surface adsorption sites on the particles. Extended x-ray absorption fine structure (EXAFS) results revealed binding site details as a function of pH and particle size and will be presented.

Application of XAS technique for the purpose of gaining insights into the mechanisms of interaction between hematite nano particles and heavy metal cadmium suggests a first step towards alleviating nano particle related environmental and health hazards.

C-22

## Integrated Photonics with Single-layer MoS<sub>2</sub>

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Two-dimensional transition metal dichalcogenides (TMDCs) such as MoS<sub>2</sub> are direct band gap semiconductors at the limit of atomic-scale thickness. The strong optical transitions across the direct band gap of monolayer TMDCs suggest that atomically thin 2D semiconductors can be useful materials for interfacing with photonics to achieve new device functionality. We report on the integration of MoS<sub>2</sub> monolayers with silicon nitride microresonators assembled by visco-elastic layer transfer techniques. Coupling between the photonic mode and the monolayer semiconductor flakes is confirmed by reduction of the quality factor. This achievement paves the way for functional integrated optoelectronic devices such as modulators that harness the optical properties of 2D semiconductors.

## Technique

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C-20

### **Microfabrication of All-copper Waveguides by UV-lithography**

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In order for radar systems to see through clouds at video frame rates, the frequency of transmission must be much higher than radio frequency, and the transmission power must be high to enable video rate. As frequency increases, waveguide feature structure dimensions and tolerances decrease. Submicron precision and surface finish are needed in order to achieve the required power performance of the circuits. Thermal management of high radiation power is needed for stable continuous operation, which can only be achieved with an all-copper structure for the waveguide.

We report the fabrication of two-level all-copper folded waveguide circuits. The fabrication method is based on UV-lithography using SU-8 negative photoresist, followed by copper electroforming. The method achieved the necessary dimensional accuracy, smooth vertical side walls, low fabrication cost, and all-copper structure suitable for high power applications.

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